

AD-A162 020 NEW APPROACHES TO THE SYNTHESIS OF FLUOROCARBONS(U)
IOWA UNIV IOWA CITY DEPT OF CHEMISTRY D J BURTON
01 OCT 85 AFOSR-TR-85-1027 AFOSR-84-0245

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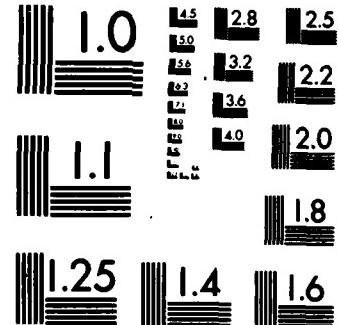
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This grant was issued under the DOD University Research Instrumentation for the purpose of upgrading equipment at the universities in order to perform research in support of National Defense. The instrument acquired was a Jeol FX-90Q(II) Fourier Transform (FT) Multi-Nuclear Magnetic Resonance Spectrometer System with the "Omni Probe." The instrument also contains variable temperature observation, internal and external lock systems and computer control of irradiation frequencies.

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New Approaches To The Synthesis of Fluorocarbons

Final Report

AFOSR-84-0245

Donald J. Burton

September, 1985

University of Iowa

Air Force Office of Scientific Research

15 July 1984 - 14 July 1985

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Research Report:

I. Statement of Problem:

This grant was issued under the Department of Defense (DOD) - University Research Instrumentation Program (FY 1984/1985) for the purpose of upgrading the University Research Instrumentation in order to improve the capability of Universities to perform research in support of National Defense. Specifically, it is a program of support for the acquisition of research equipment for the stimulation and support of basic research underlying the technology goals of DOD.

II. Instrumentation Acquired:

The instrument acquired was a Jeol FX-90Q(II) Fourier Transform (FT) Multi-Nuclear Magnetic Resonance Spectrometer System with the "Omni Probe". The instrument also contains variable temperature observation, internal and external lock systems and computer control of irradiation frequencies. A complete description (with initial cost quotations) is given on the next page.

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Chief, Technical Information Division

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III. DETAILED LIST OF EQUIPMENT WITH ESTIMATED COSTS

*Jeol FX-900(II) Basic System:	\$ 106,000
Includes Basic Broad Band System with frequency synthesizer, 10 mm broad band sample insert and probe modules. Deuterium/Lithium internal and deuterium external lock	
"Shimplex" Control of C and Y field gradients (Model No. 4-SP) for optimization of resolution by simultaneous control of the Y and curvative current shims	\$ 2,600
High Band 5 mm VT Insert (Model No. 4-BBI-10) - for use with small and/or dilute samples	\$ 990
Temperature Controller (Model No. 4-PVT) and water chiller (Model No. 4-R-W) - for low temperature work and field stability	\$ 7,475
Quiet Box Air Compressor (Model No. 4-AC)	\$ 575
Room Setup Costs (wiring, water lines, air, power, etc.)	\$ 6,000
<hr/> Total	\$ 123,640
<hr/> University Cost Sharing	\$ 39,000
<hr/> Total Requested from DOD	\$ 84,640

*See additional description (detailed) of basic system on the next page.

Source of Equipment and Contact: Peter J. Patterson (201-272-8820)
Sales Manager, Analytical
Instruments Division
Jeol, U.S.A. Inc.
235 Birchwood Avenue
Cranford, New Jersey 07016

JEOL-JNM/FX-90Q
HIGH RESOLUTION FOURIER TRANSFORMATION
MULTI-NUCLEAR MAGNETIC RESONANCE SPECTROMETER SYSTEM

Basic System Includes:

- Proton observation at 90 MHz; Carbon at 22.5 MHz
- "Omni-Probe Perma Body" with plug-in insert, probe and irradiation modules
- Console w/diagnostic monitoring & service indicator lights
- Digital Quadrature Detection System
- Four-channel digital Phase Shifters
- Broad-Band r.f. amplifier
- Phase Lock of all r.f. channels & phase shifters
- Time shared deuterium internal lock with lock monitor
- Proton Homo/Hetero Nuclear Multi-Mode Gated Spin Decoupler
- Homospoil generation
- 50 KHz ADC for acquisition of 50 KHz spectral width
- Foreground/Background w/Multi-task Automatic Priority Set
- Micro-processor controlled PROGRAMMABLE MULTI-PULSE GENERATOR with 13 channel output (PG-200)
- X-Y flat bed recorder
- Alphanumeric printer/microprocessor system
- Dual Floppy Disc unit 250 K, 16 bit word
- Light Pen Control System (LPCS) with DRT for alphanumeric display, data display and setting of operating parameters
- Data Processing System w/16K for data acquisition includes:

12 bit AD/DA (2 channel)	CPU with 40,960 words total
Auto Error Correction	CPU expandable to 65 K words
- B1-level software package—isolates pre-programmed routine operation from comprehensive hi-level operation
- 2-D Spectroscopy Program

- Systems check programs
 - Comprehensive auto-run system with programmable multi-stack capability
 - High dynamic range double precision (32 BIT) acquisition and FFT
 - Wide gap electromagnet with power supply and magnet water heat exchanger
(water to water system)
 - Starter kit: 500 sheets of calibrated chart paper, 5 NMR tubes, 5 vortex plugs,
3 standard samples (10 mm) and 3 pens

III. Instrument Capability:

This instrument has allowed us to pursue research projects in fluorine chemistry not accessible to us without multi-nuclear NMR capabilities.

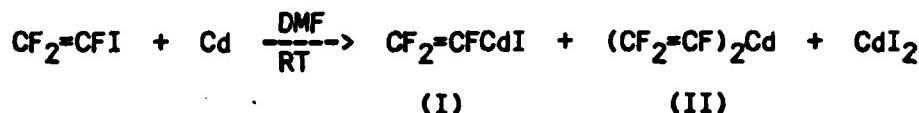
Some of these projects are summarized below:

[A]: Preparation of Perfluoroalkenyl Cadmium Reagents:

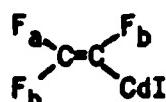
Cadmium has two NMR active isotopes, ^{111}Cd and ^{113}Cd with spin of 1/2. Thus, incorporation of cadmium into organic substrates can be utilized to determine structural information about the resultant cadmium-containing moiety.

Thus, we have prepared fluorine-containing alkenyl cadmium reagents via reaction of fluorooiodo alkenes with activated cadmium powders.

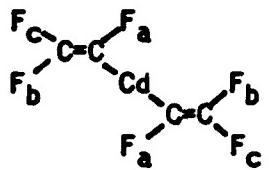
For example:



This reaction produces a mixture of the mono cadmium reagent (I) and the bis cadmium reagent (II). This ratio is solvent dependent. Assignment of structure to (I) and/or (II) is readily accomplished via observation of the ^{113}Cd NMR spectrum of the reaction mixture.

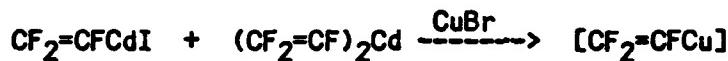


(I) ^{113}Cd spectrum is a doublet of doublet of doublets



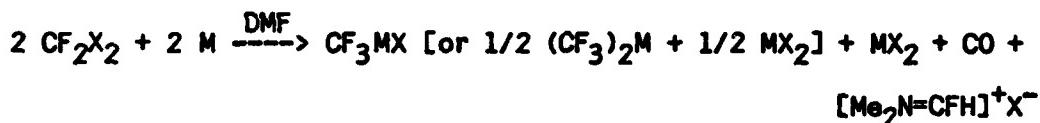
(II) ^{113}Cd spectrum is triplet of triplet of triplets

Thus, it's quite easy to determine the structure of these organometallics. Metathesis of these reagents with Cu(II) salts then provides us with an entry to the hitherto unknown - but synthetically interesting - copper reagents.



[B]: Preparation of Trifluoromethyl Organometallics Directly from Freons:

We have discovered a new, novel, and unprecedented conversion of a difluorodihalomethane directly (with metal powders) to a trifluoromethyl organometallic. For example:



X = Br, Cl M = Cd, Zn

This remarkable reaction thus permits direct preparation of trifluoromethyl cadmium and zinc reagents from cheap, commercially - available Freons.

These trifluoromethyl organometallics are a mixture of mono, CF_3CdX (I), and bis reagents, $(\text{CF}_3)_2\text{Cd}$ (II). Again, the use of ^{113}Cd NMR permits us to unequivocally assign the structures to these species:

CF_3CdX (I) : ^{113}Cd NMR is a quartet

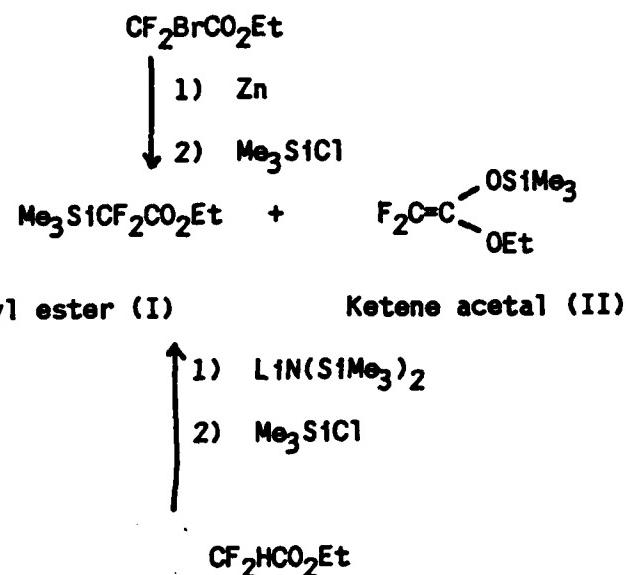
$(\text{CF}_3)_2\text{Cd}$ (II) : ^{113}Cd NMR is a heptet.

It's important to know the ratio of I/II - which is solvent dependent - since the reactivity of these moieties is not identical in all reactions.

and conditions (for best results) must be selected to maximize the moiety which is the most reactive. Without ^{113}Cd NMR capability, we would have no way to monitor the I/II ratio or the reactivity of each species in further chemical reactions. Thus, our ability to pursue and understand this reaction and these reagents is totally dependent on the NMR capability.

[C]: Ketene Silyl Acetals:

We have recently initiated a project to produce fluorinated ketene acetals. These reactive intermediates can then be utilized to introduce fluorinated functionalized units into organic molecules. Two modes of generation of these species have thus far been employed. As noted in the example below, one can obtain either the ketene silyl acetal or the carbon silylated ester.



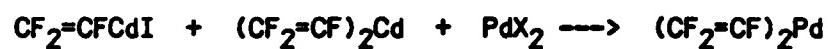
The formation of (I) and/or (II) is dependent upon the mode of generation.

The structural assignment of (I) and/or (II) can only be unambiguously made via ^{29}Si NMR. Silicon has an NMR active isotope (only 4.70% natural abundance) with spin 1/2. Thus, it's difficult to obtain such spectra of ^{29}Si unless one has access to an FT-Multi-Nuclear instrument.

Observation of the ^{29}Si spectrum of (I) or (II) easily permits structural assignments. (I) Shows ^{29}Si -F coupling of 22-30 Hz whereas (II) shows ^{29}Si -F coupling of ≈ 0 . Therefore, the use of our Jeol FT-90(Q) instrument allows us to pursue a problem hitherto unavailable to us.

[D]: Preparation of Transition Metal Fluorine-Containing Organometallics:

As noted in Parts I and II above, we have now developed a useful entry to both saturated and unsaturated organocadmium reagents. These reagents, as indicated, readily undergo metathesis reactions. Preliminary results with salts of Ag, Rh, Pd, Pt, Cu, and Co indicate we can utilize such metathesis processes to gain an entry to these fluorinated transition metal moieties - that cannot be made via direct reaction. For example:



In the case of Ag, Rh, Pd, and Pt (which have naturally occurring NMR active isotopes) we can utilize these isotopes to again obtain structural and characterization information. Thus, this newly acquired capability has allowed to initiate new projects in the area not previously accessible.

IV. Instrument Utilization:

The instrument was installed in May, 1985. The original delivery date was scheduled for March 1985 - however, delays (from Jeol) postponed delivery and installation until May.

After testing of the equipment by ourselves and training of my students for hands on use, the instrument was opened to access by all students and post-docs on June 4, 1985.

Between June 4 and September 1, 1985, a total of 1,663 samples were analyzed with this instrument. Thus, approximately 555 spectra per month were recorded with this new instrument. As additional parameters for new nuclei are added this access pattern will probably increase somewhat. We estimate that approximately 600 samples per month will be analyzed with this spectrometer.

V. Budget Summary:

Instrument Cost (including shipping) ^a :	\$110,993.96
Room set-up cost ^b	\$ 2,714.99
<hr/>	
Total Costs	\$113,708.95

- (a) Instrument cost is less than original quote - since we persuaded Jeol to grant us an educational discount.
- (b) Includes wiring, water lines, power, air lines - actual cost is less than original estimate since we installed the water lines and air lines ourselves rather than pay our Physical Plant to install them.

University Contribution: \$39,000

Total Cost to AFOSR: \$113,708.95 - \$39,000 = \$74,708.95

Amount Funded by AFOSR: \$84,640

Amount of Excess AFOSR Funds: \$84,640 - \$74,708.85 = \$9,931.05

VI. Excess Funds:

As noted in the Budget Summary we were able to save \$9,931.05 from the original instrument quotation and room set-up costs. These savings were possible via:

- (a) Educational discount from Jeol on the spectrometer
- (b) Installation of water and air lines by ourselves rather than University personnel.

VII. Disposition of Excess Funds:

The excess AFOSR funds can be:

- (a) returned to AFOSR
- (b) utilized for maintenance of the spectrometer.

Since this instrument is basically used for our fluorocarbon research, the department will not support maintenance - hence we are responsible for all maintenance costs. Thus, we would like to request that the savings

incurred (via our efforts) be utilized to provide initial maintenance costs for the spectrometer - thereby leaving the excess funds with the University in a maintenance account.

If the above request cannot be honored, the University will refund (by check) the excess funds to AFOSR.

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